

Supporting information for

A recyclable disulfide bond chemical cross-linking high toughness, high conductivity ion gels based on re-shaping and restructuring in gel state

1 Chemical and Materials

All commercially available reagents were used as received unless otherwise noted. Poly (ethylene oxide) (PEO) ($M_n = 35\text{kDa}$, $D = 1.04$) was purchased from Sigma-Aldrich and dehydrated by freeze drying before use. 1-ethyl-3-methylimidazolium bis-(trifluoromethyl) sulfonyl amide ([EMI][TFSA], ionic liquid), Propargyl bromide (80% solution in toluene), Pentamethyldiethylenetriamine (PMDETA, 99%), 4-Methylbenzyl chloride (99%), Benzyl azide (97%) and 4-vinylbenzyl chloride (VBC) were purchased from Aladdin-Reagent. All the other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Styrene (St) was purified by distilled under reduced pressure and 4-vinylbenzyl chloride (VBC) was passed through activated alumina columns prior to use. Dichloromethane, triethylamine were dehydrated before use.

2 Analyses

Mass spectrum data were obtained by using a Thermo LTQ instrument operated in electrospray ionization (ESI) mode, and only positive spectra were showed. Other measurements were performed according our previous work.¹

3. Synthesis

Preparation of ion gel

The ion gels were prepared according the procedure in our previous work,¹ except the polymerization temperature and time for SOS-Cl. In this work, after obtain a homogeneous solution, the solution was then immersed in an oil bath thermostated at 140 °C and polymerization was allowed to proceed for 60 minutes.

Synthesis of disulfide 1

In a typical experiment, benzyl azide (0.20 g), PMDETA (80.0 mg), O-ethyl-S-prop-2-ynyl Carbonodithio-ate (0.25 g), CuI (60.0 mg) was dissolved in DMF (10 ml). The mixture was kept stirred at room temperature for 24 h. Then the reaction mixture was poured into 50 mL of brine and the resulting precipitate was filtered and dried. The raw product was purified by column chromatography on silica gel (CH₂Cl₂: ethyl acetate =100: 1) to give a brown solid.

The above product (about 0.15g), 0.25 ml of butyl amine, was dissolved in CH₂Cl₂ (10 ml) and then the mixture was kept stirred at room temperature for 1.5 h. After the solvent was removed under vacuum, 6 ml of DMF, PMDETA (60 mg) and CuI (40 mg) was added and the mixture was kept stirred at room temperature for 36 h. Then the reaction mixture was poured into 50 mL of brine and the resulting precipitate was filtered. After dried under vacuum, the disulfide 1 was obtained as a white powder. ¹H-NMR of disulfide 1 (in CDCl₃) is showed in Fig. S4 (top). ESI-MS (Fig. S6a): m/z calcd for C₂₀H₂₀N₆S₂:408.54; found: 409.06 [M+H]⁺.

Synthesis of disulfide 2

In a typical experiment, 4-Methylbenzyl chloride (0.41g), NaN₃ (0.25g) were dissolved in 7 ml of DMF, and then the mixture was kept stirred at 80 °C for 3h. Then the reaction mixture was poured into 50 mL of brine and the resulting precipitate was filtered and dried. Then PMDETA (100 mg), O-ethyl-S-prop-2-ynyl Carbonodithio-ate (0.45 g), CuI (80.0 mg) and 10 ml of DMF were added. The mixture was kept stirred at room temperature for 24 h. Then the reaction mixture was poured into 50 mL of brine and the resulting precipitate was filtered and dried. The raw product was purified by column chromatography on silica gel (CH₂Cl₂: ethyl acetate =100: 1) to give a brown solid.

The above product (about 0.15g), 0.25 ml of butyl amine, was dissolved in CH₂Cl₂ (10 ml) and then the mixture was kept stirred at room temperature for 1.5 h. After the solvent was removed under vacuum, 6 ml of DMF, PMDETA (60 mg) and CuI (40 mg) was added and the mixture was kept stirred at room temperature for 36 h. Then the reaction mixture was poured into 50 mL of brine and the resulting precipitate was filtered. After dried under vacuum, the disulfide 1 was obtained as a white powder. ¹H-NMR of disulfide 2 (in CDCl₃) is showed in Fig. S4 (bottom). ESI-MS (Fig. S6b): m/z calcd for C₂₂H₂₄N₆S₂: 436.60; found: 437.12 [M+H]⁺.

Model disulfides metathesis reaction

Model 1 (in DMF with copper salt): in a typical experiment, disulfide 1 (12.0 mg), disulfide 2 (14.0 mg), PMDETA (6 mg), CuI (2 mg) was dissolved in 2 ml of DMF, and then the mixture were kept stirred at 60 °C for 24 h. After

that, the reaction mixture was poured into 20 mL of brine and the resulting precipitate was filtered and dried. The product was marked as product 1.

Model 2 (in IL without copper salt): in a typical experiment, disulfide 1 (12.0 mg), disulfide 2 (14.0 mg) was dissolved in 2 ml of IL, and then the mixture were kept stirred at 60 °C for 24 h. Because it was difficult to separate the product from the IL, the reaction mixture was directly used to perform ESI-MS measurement. The product was marked as product 2.

Model 3 (in IL with copper salt): in a typical experiment, disulfide 1 (12.0 mg), disulfide 2 (14.0 mg), PMDETA (6 mg), CuI (2 mg) was dissolved in 2 ml of IL, and then the mixture were kept stirred at 60 °C for 24 h. Because it was difficult to separate the product from the IL, the reaction mixture was directly used to perform ESI-MS measurement. The product was marked as product 3.

4 Supporting figures and tables

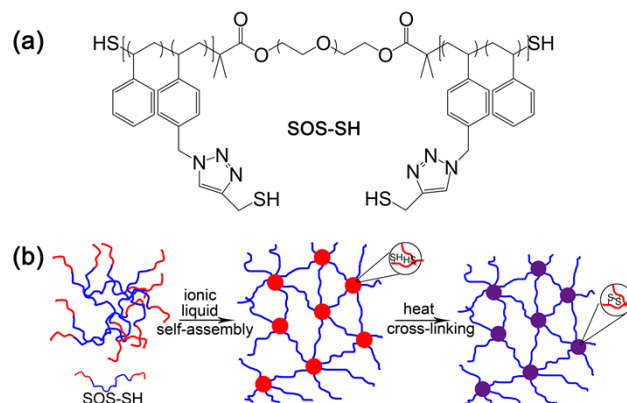


Fig.S1 (a) Chemical structure of the ABA type triblock copolymer, SOS-SH; (b) Schematic preparation procedure of disulfide bond cross-linking ion gel combining self-assembly of ABA type triblock copolymer in ionic liquid and reversible chemical cross-linking together.

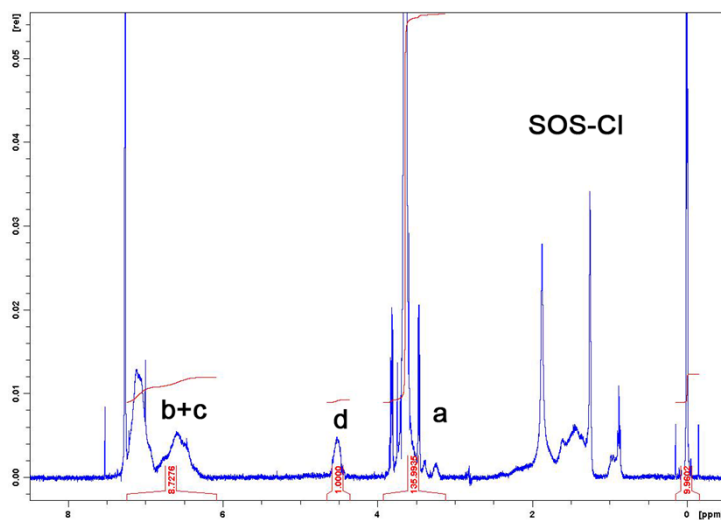


Fig. S2 Integration of peaks a, b+c and d of $^1\text{H-NMR}$ spectra of triblock copolymer SOS-Cl of 60 min.

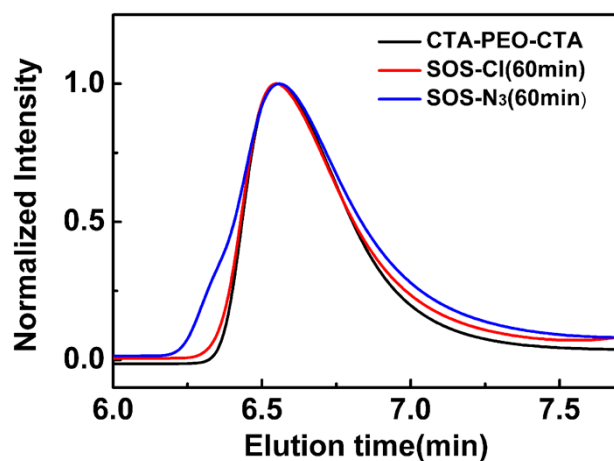


Fig. S3 Gel permeation chromatography (GPC) traces of CTA-PEO-CTA, SOS-Cl and SOS-N₃ of 60min.

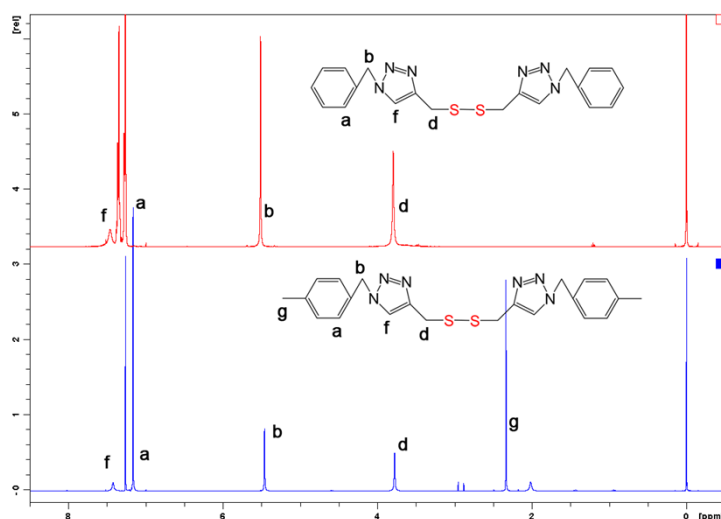


Fig. S4 ¹H-NMR (in CDCl₃) of disulfide 1 (top) and disulfide 2 (bottom).

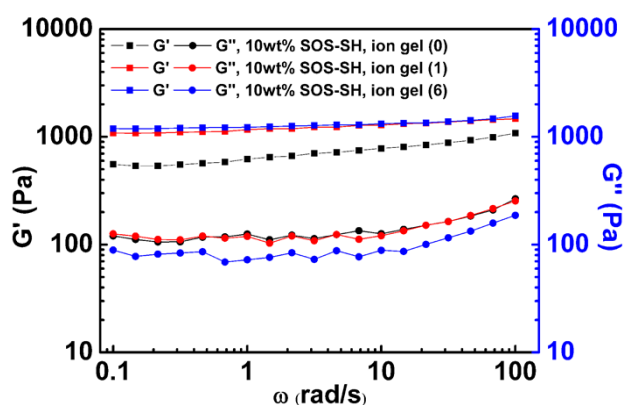


Fig.S5 Variations of storage modulus (G') and loss modulus (G'') as functions of angular frequency (ω) at 100 °C for original cross-linking (ion gel (0), black), first reforming (ion gel (1), red), sixth reforming (ion gel (6), blue) 10wt% SOS-SH ion gels. The numbers (0, 1, 6) in the brackets indicate the time of broken-restructuring-reshaping cycle.

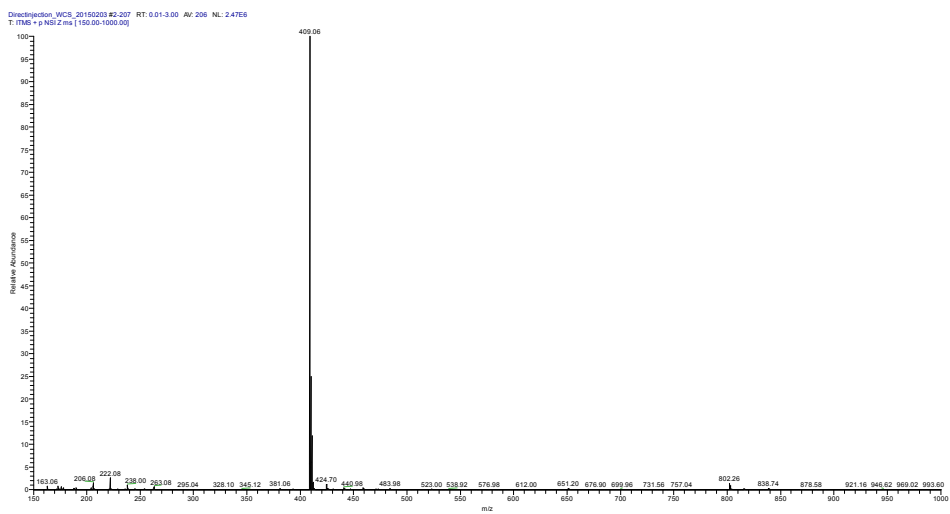


Fig. S6a ESI-MS (positive) of disulfide 1.

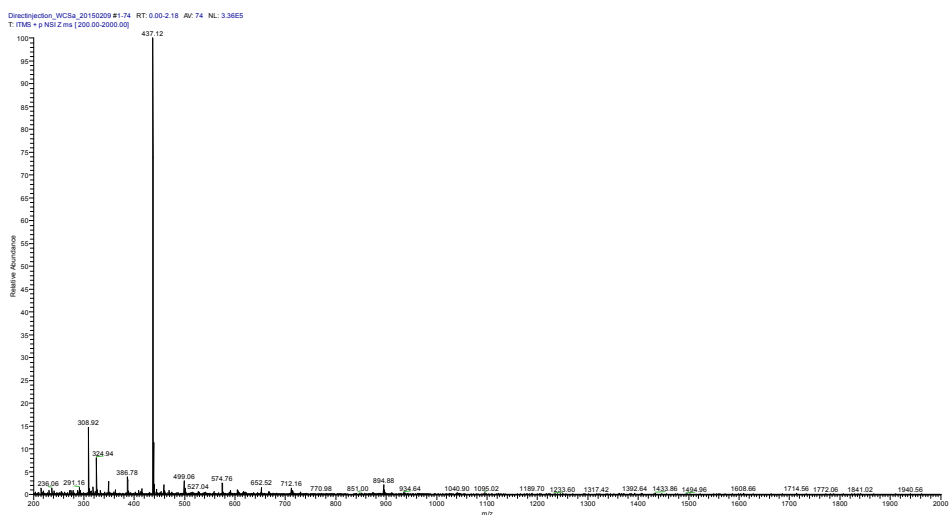


Fig. S6b ESI-MS (positive) of disulfide 2.

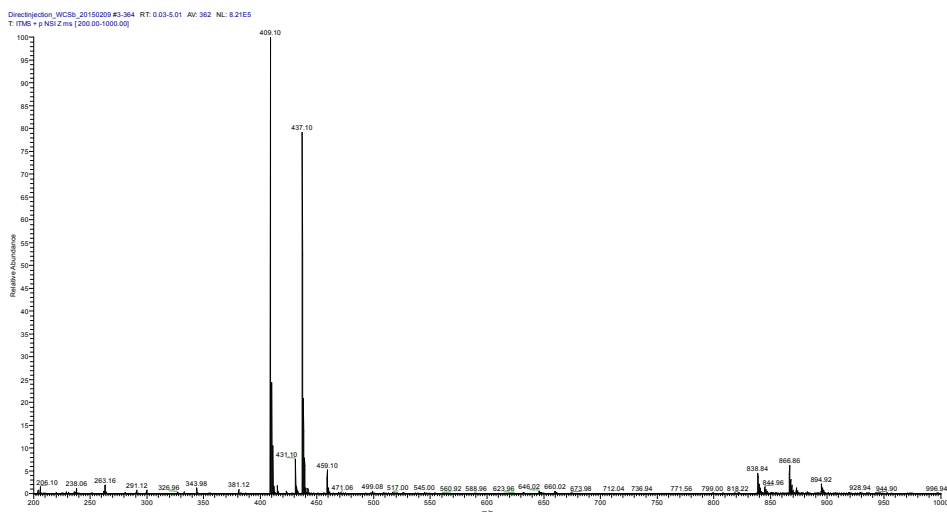


Fig. S6c ESI-MS (positive) of product 1 (in DMF with copper salt).

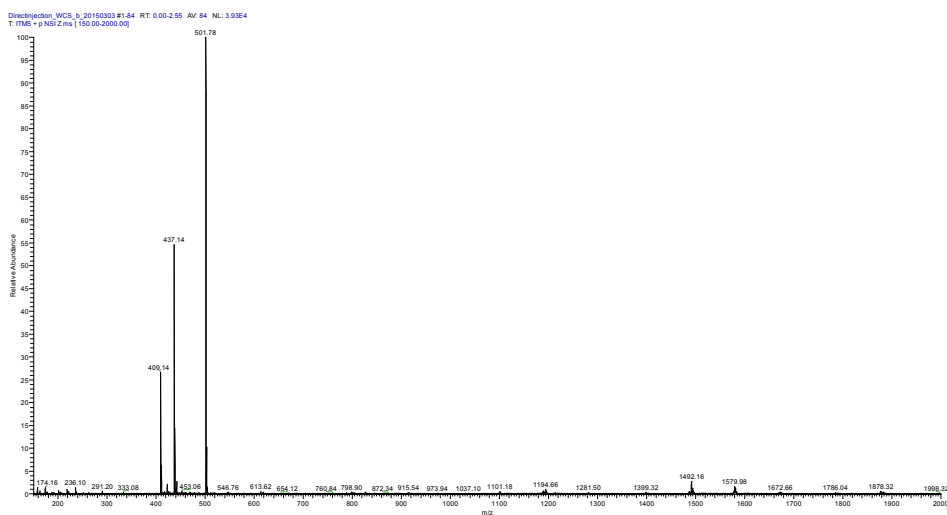


Fig. S6d ESI-MS (positive) of product 2 (in IL without copper salt).

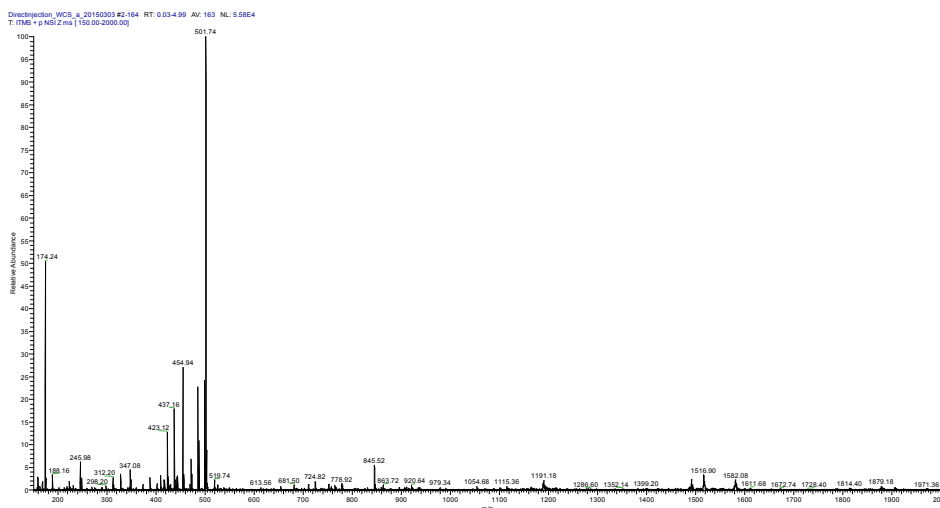


Fig. S6e ESI-MS (positive) of product 3 (in IL with copper salt).

	average tensile strength (kPa)	average ultimate elongation
Ion gel (0)	30.2	5.1
Ion gel (1)	66.4	4.3
Ion gel (6)	61.1	4.2

Table.S1 Results of tensile tests for ion gel (0), ion gel (1), ion gel (6) at room temperature. The numbers (0, 1, 6) in the brackets indicate the time of broken-restructuring-reshaping cycle.

Table.S2 Mn and PDI of CTA-PEO-CTA, SOS-Cl and SOS-N₃

Polymer	Mn (kDa) poly (St-co-VBC)	Mn (kDa) PEO	PDI
CTA-PEO-CTA	/	35	1.17
SOS-Cl	2.4 ^a	35	1.21
SOS-N ₃	2.4	35	1.28

^aThe Mn of each end-block.

1. C. Wei, M. Chen, D. Liu, W. Zhou, M. Khan, X. Wu, N. Huang and L. Li, *RSC Advances*, 2015, **5**, 22638-22646.